THE LATENT HEAT OF VAPORIZATION OF LIQUID OXYGEN-NITROGEN MIXTURES.

BY LEO I. DANA.

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INTRODUCTION.

This research deals with the determination of the latent heat of vaporization at atmospheric pressure of liquid oxygen, nitrogen, and of mixtures of the two in all proportions. The best of the previous determinations for pure oxygen and nitrogen and those reported herewith are listed in Table I.

TABLE I.

OXYGEN.

Investigator		Latent Heat
J. S. Shearer [1]	1903	59.5
T. Estreicher [2]	1904	57.8
I. Dewar [3]	1906	51.1
H. Alt [4]	1906	50.92
H. Barschall [5]	1911	51.3
W. H. Keesom [6]	1914	50.8
L. I. Dana	1922	51.01

NITROGEN.

J. S. Shearer [1]	1903	49.8
I. Dewar [3]	1906	50.4
H. Alt [4]	1906	47.65
L. I. Dana	1922	47.74

[1] Phys. Rev., **17**, 469, 1903.
[2] Bull. de l'Acad. des Sc. de Cracovie, p. 183, 1904.
[3] Proc. Roy. Soc., **76** A, 325, 1906.
[4] Ann. der Phys., **19**, 739, 1906.
[5] Zeit. für Elektrochemie, **17**, 345, 1911.
[6] Comm. Phys. Lab. Leiden, No. 137e, 1914.

The general method adopted by the above-mentioned investigators was to pass an electric current through a coil immersed in a Dewar flask filled with the liquid. By measuring the power input, and the amount of liquid evaporated, either from the volume of the gas or the weight of the liquid, the latent heat could be evaluated. Dewar dropped a mass of metal of known specific heat into the liquid and measured the volume of the evaporated gas. In all the cases except those of Alt and Barschall, the heat leaks were large. As Alt pointed out, the evaporation due to conduction down the current leads, while the evaporation proceeded, was obviously not the same as that without power input.

Several attempts[7, 8, 9] have been made to measure the latent heat of mixtures by methods identical with those used for pure substances. None of the results, however, can be said to possess definite meaning. In the first place, no accurate thermodynamic definition of the latent heat was given or followed; it is possible to define the latent heat of a binary mixture in several ways. Secondly, the method of placing a heating coil in a large volume of the liquid mixture and evaporating without stirring cannot yield definite results. The reason for this is that the changes of composition which take place in one portion of the liquid (say near the heating coil) are not communicated to all portions except by slow convection. In such an instance, not only would the existence of a steady state be improbable, but the results would depend on the position of the heating coil.

The calorimetric method adopted in this research is the method of continuous flow. The principal feature of the calorimeter consists of the thermal isolation of a small volume of the liquid by means of a glass bulb, surrounded by a vacuum jacket, communicating with a large volume of the liquid through a capillary tube. See Figures 1 and 2. Heat is supplied electrically through a heating coil in the bulb. Issuing from the top of the latter is a narrow glass tube through which the cold gas from the boiling liquid flows with so high a velocity that the main source of heat leak — conduction down the heating coil leads — is diminished to a negligible proportion. When a binary mixture is being evaporated, the important property of the calorimeter to be noticed — assuming that the proper steady state exists in the bulb — is that the composition of the vapor arising from it is identical with that of the main body of liquid in the outside bath.

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7 J. S. Shearer, Phys. Rev., 17, 469, 1904.
8 Fenner and Richtmyer, Phys. Rev., 20, 77, 1905.
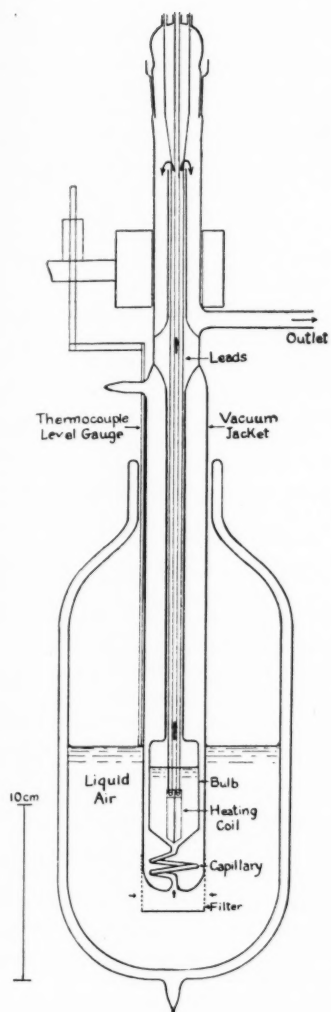9 G. Witt, Archiv für Matematik, Astronomi och Fysik, Upsala, 7, No. 32, 1, 1911–12.
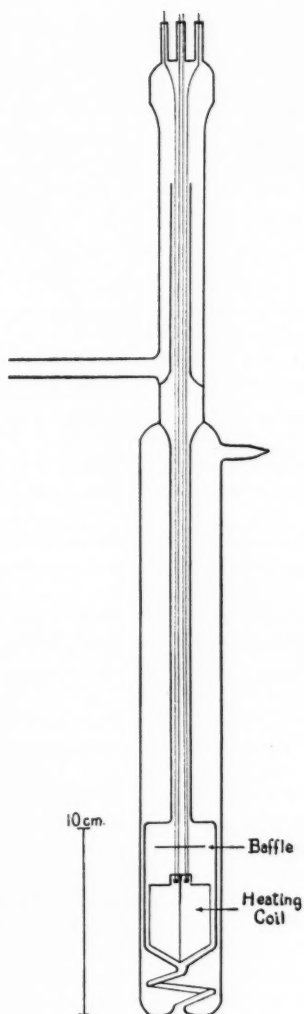
Fig. 1.

Fig. 2.

Power is measured by determining the current and voltage with a high precision potentiometer. After the evaporated gas passes through a circuit which saturates it with water vapor and brings it to a definite temperature, its volume is measured by a laboratory gas meter of the wet type which has afforded a fairly high degree of precision. A chronograph records the rate of rotation of the meter drum. As the liquid evaporated, the calorimeter was lowered by a special mechanism, thus maintaining a constant level of liquid in the bulb.

Definitions of the Latent Heat.

There is no need to enter into detail concerning the definition of the latent heat of vaporization for a pure substance. For a binary mixture, however, the definition is a far more complicated matter, since in addition to three fundamental variables such as pressure, temperature, and volume, there is also the composition; thus one would expect a number of definitions equal to the number of possible methods of evaporation.

Consider the temperature-composition diagram for mixtures of liquid oxygen and nitrogen at constant pressure, Figure 3. The composition x represents the actual mole-fraction of oxygen which (as far as the perfect gas laws may be considered to hold for the gases under normal conditions) is equal to the per cent of oxygen by volume as determined by ordinary gas analysis. One definition of the latent heat is the heat required to evaporate an infinitesimally small amount from a pool of liquid of composition x_1 at constant temperature and pressure, into the vapor phase x_2 normally in equilibrium with the liquid.[10, 11] Two other definitions result from the method of beginning with a liquid of composition x_1, and evaporating the liquid completely — in the first case, at constant temperature, and in the second, at constant pressure. The latent heat determined in this investigation can be called the latent heat at constant composition, or the vertical instead of the horizontal latent heat. That is (looking at Fig. 3), the change of state is from the liquid state 1 to the vapor state 1' and the heat per unit mass supplied to the liquid measures the total change in heat-content in passing from the state 1 to 1'. By the heat-content is meant the thermodynamic function $H = E + pv$, where E is the internal energy, p the pressure, and v the specific volume.

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10 v. d. Waals-Kohnstamm, Lehrbuch der Thermodynamik, Band II, p. 112.
11 J. P. Kuenen, Verdampfung und Verflüssigung von Gemischen, p. 38.

How the process of evaporation can be carried out in the calorimeter seems at first sight somewhat obscure, and we will attempt to describe it in more detail. As stated before, the composition of the vapor leaving the bulb is the same as that of the liquid entering the capillary from the outside bath, provided that a steady state has been reached in the bulb and that no liquid or vapor is ejected back into the bath. This fact was verified by experiment: first, by analysis of the liquid
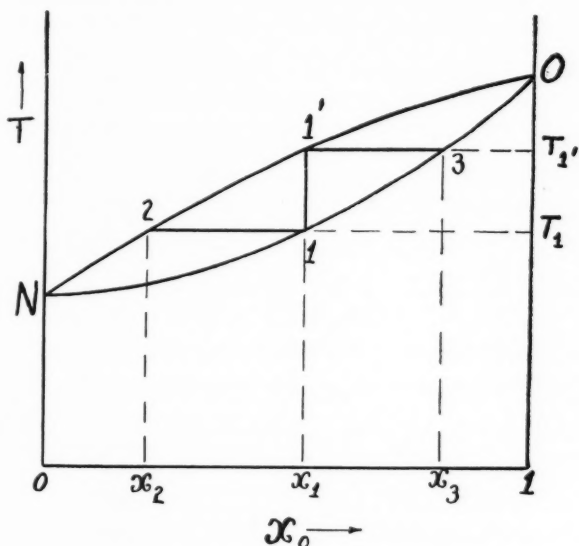
Fig. 3.

and vapor, and second, by weight of the separate components before mixing. This condition must hold if the law of conservation of matter holds, but it seems paradoxical in view of the fact that the vapor boiling off from a binary mixture is, in general, of different composition from the liquid. Nevertheless, if we take the composition of the liquid in the bath as x_1, it is evident (Fig. 3) that the vapor which normally would come off from this liquid would be of composition x_2, but, since the vapor issuing from the bulb is of composition $x_{1'} = x_1$, the liquid in the bulb must be x_3. This is actually the case. As the liquid x_3 in the bulb loses vapor x_1, which is richer in nitrogen than x_3

liquid x_1, also richer in nitrogen than x_3, enters from the capillary to make up for the loss. The temperature of the liquid in the bulb is always higher than that of the outside liquid by an amount given by the vertical ordinate between the two curves in Figure 3.

For this method to work it would seem to be necessary that the bulb be reasonably small and that good stirring of the liquid take place in order that a steady state should be attained in a short time. In our case, sufficient stirring was produced by the boiling. A test of the correctness of the conditions in the bulb is furnished by observing whether the composition of the vapor arising from it is independent of the rate of evaporation. One of the main difficulties was to produce this result. Obviously, this state of affairs is not sufficient for constancy of the apparent or measured latent heat with the rate of evaporation, for the heat leaks or other disturbances may be different at different rates.

DESIGN OF THE CALORIMETERS.

The principles and factors governing the design of the calorimeters will now be considered. A number of models were constructed of which three were used for final data. In Table II the dimensions in cm. of the important parts are given.

TABLE II.

| Calor. no. | Bulb | | Capillary | |
	Length	Diameter	Length	Inside diameter
III	5.5	3.3	13	0.25
VI	5.0	2.8	20	0.13
VII	7.0	3.5	15	0.13

Pyrex glass was used for the calorimeters. In order to reduce the amount of waste liquid at the end of each run, the bulb was placed as low as possible in the jacket. The inside of the jacketed space was silvered and evacuated to cut down convection and radiation. The use of a narrow tube for conveying the evaporated gas resulted in a high velocity of flow, thus diminishing the heat conduction down the copper leads. The tube was of length adequate to make negligible the conduction down the glass. As shown in Figures 1 and 2, the cold gas passed through a circuitous path at the top of the calorimeter so that its cooling power could be utilized.

As the largest heat leak encountered is the heat conduction down the copper leads the diameter had to be chosen as small as consistent with

low development of Joulean heat in the leads. The currents were of
the order of one ampere. Number 28 copper wire seemed to be the
best compromise. The wires, insulated over their whole length by
very fine, long, glass capillaries, were soldered to heavy copper termi-
nals, enclosed by tubes at the head. For potential leads, Number 30
constantan, also insulated with glass capillaries, was chosen. The
resistance of these leads had to be taken into account in the potential
measurements, and did not vary appreciably with the temperature.

It is to be observed that the measurement of the conduction leaks
must be made while the calorimeter is running, for the cooling power
of the cold gases is intended to take care of these leaks. A thermo-
couple, with one junction in the liquid, was installed along the central
tube of the calorimeter. One element of the couple was copper, of the
same diameter as that of the leads to the heating coil; fine constantan
wires were soldered to the copper 10 cm. apart, and the e.m.f.'s were
read with the power on. At a power input of 8 watts the junction
10 cm. above the liquid read 6° C higher than the liquid, and at 20
watts it read 2.5° C higher. Now if we assume, at worst, the tempera-
ture gradient to be linear from 10 cm. above to the surface of the
liquid, the conduction down the glass tube is not more than 1 part in
10,000 of the power input, and that down the copper leads is at most
3 parts in 10,000. The possibility has also to be considered that a
part of the Joulean heat developed in the leads can enter the liquid;
rough calculations show that it is not more than 2 parts in 10,000.
Corrections have been applied for these leaks, although, as far as the
accuracy to which the final data is given, they may well have been
omitted.

With pure oxygen and nitrogen the temperature in the bulb is the
same as that outside in the bath; thus, in these cases, there is no
question of radiation to the lower half of the calorimeter. Approxi-
mate calculations show that radiation from above is negligible. The
results for the latent heats with calorimeter VI were the same when
silvered or unsilvered, even with mixtures. But calorimeter VII
showed a small effect with mixtures due to radiation to the surround-
ings, which calculation evinced to be possible as regards order of
magnitude; on silvering the effect disappeared. As a control on the
losses through the vacuum by radiation, convection, and glass con-
duction, the leads and heating coil were removed immediately at the
close of a run, and the attempt was made to collect any gas evolved,
but no appreciable quantity came off.

The same heating coil served for calorimeters III and VI. The

leads to the coil were attached to the ground glass stopper head at the top — surrounded by a mercury cup — and the whole combination formed a unit which could readily be removed. In calorimeter VII, however, the heating coil was sealed into the bulb so that the whole calorimeter formed one piece, as shown in Figure 2. The heating coil for calorimeters III and VI consisted of about 55 cm. of number 35 B. and S. gage manganin wire, having a resistance of about 15 ohms. It was strung with glass beads and wound closely on a mica frame — the coil having a final diameter of about 1.2 cm. and a length of 3.0 cm. The glass beads served the double purpose of insulation and the production of quiet boiling. Previous investigators found that the power input with a bare wire was sharply limited. With our coils, however, the beads prevented bumping, and the boiling remained quiet and regular even with powers as high as 20 watts. Although the data obtained with the first coil with various rates of evaporation indicated that very little, if any, superheating of the vapor or spattering of the liquid existed, nevertheless, the fear arose that such difficulties might occur with so concentrated a heating coil. Therefore, the heating coil for calorimeter VII had quite different constants. It was made considerably longer — 125 cm., 16 ohms resistance — and was distributed on a mica frame throughout the volume of a larger bulb. The wire was completely covered with small pyrex glass beads with sharp edges. If there was superheating of the liquid or of the vapor, it should be considerably less with such a coil than with the previous coil. At the same time, the mica baffle plate, which remained fixed above the heating coil, should reduce to some extent the spattering if it existed in appreciable amount. Fortunately the results with both types of calorimeter were identical within the experimental error. As a check against superheating of the liquid, the temperature in the bulb, while evaporating liquid oxygen, was observed to be the same, within 0.01° C, as that of the liquid outside; and, as a check against superheating of the vapor, it was found that with oxygen the same value of the latent heat resulted when the level of the liquid stood at the top of the heating coil as when it stood 1.5 cm. above. In several cases, in which, by accident, the heating coil remained only partly immersed, very much higher values for the latent heat than normally found were recorded.

In determining the proper dimensions of the capillary, we have to take into account a number of considerations. Since with mixtures the temperature in the bulb is higher than in the liquid outside, the dimensions of the capillary must be such that the heat conducted away

is negligible. If the internal diameter is too large, the liquid has a tendency to kick back when the evaporation is proceeding. This was apparently the case with calorimeter III, as the composition of the vapor was not constant with the rate of evaporation, and consequently it could not be used for mixtures. To prevent the tube from becoming clogged by small particles of ice it was necessary to use a filter, just slipping over the bottom of the calorimeter. It consisted of a cylinder of fine gauze, closed at the bottom by a thin brass plate. It was not desirable to have the gauze at the bottom because the mesh sometimes allowed bubbles of gas to pass through, or the sharp points of the mesh acted as centers of formation of bubbles which found their way up to the capillary, thus introducing extra gas into the line. Finally the capillary had to be free from sharp kinks so that the flow of liquid would be perfectly regular. The velocities of the liquid through the capillary were rather high; e.g., for calorimeter VI, and for the fastest rate of evaporation (20 watts) the flow amounted to 7 cm. per second.

Liquid Levels.

It is evident that as the liquid in the bulb evaporates its level would fall quite rapidly if it were not kept constant by the influx of new liquid and by lowering the calorimeter. In maintaining the level we have first to consider the proper height of the liquid above the coil, in order that the coil should not burn out, and that the vapor should not become superheated. For safety the liquid was held 1 to 1.5 cm. above the heating coil. It requires a certain pressure head to force the gas through the pipes and meter, to overcome the resistance of the capillary to the flow of fluid, and to balance the difference of densities with mixtures when the liquid in the bulb is richer in oxygen than the liquid outside and consequently denser. The last three factors determine the natural difference in level between the outside and inside while operating. Fortunately the pressure head necessary to force the gas through the meter and tubes was not high — it varied from 0.8 to 1.6 cm. of water — for the liquid from the surface to the bottom of the filter is waste liquid as far as a run at a particular time is concerned. Assuming Poisseuille's law to hold, the pressure head required to force the liquid through the capillary can be calculated. For calorimeter VI at the maximum rate of evaporation it is about 4 mm. The correction for differences in densities depends on the compositions and densities, but the maximum effect is only 1.5 mm. A copper-constantan thermocouple, connected to a micrometer

screw, served as a level gauge. The conduction of heat along the copper was so great that when the junction rested just above the liquid surface a thermocouple millivoltmeter read slightly less than when the junction just touched the liquid. Thus, by the kick of the needle, one could tell when the junction came into contact with the surface, to 0.1 mm. For the pure components the question of the level is not of much importance, but it is vitally so for mixtures.

In the first set-up, the calorimeter was attached to a vertical screw, and whenever the millivoltmeter indicated that the liquid level had fallen, the calorimeter was lowered 0.5 mm. or so by turning the screw. With this procedure, or even with more careful hand regulation, one could not, with mixtures, maintain constant for any length of time the composition of vapor issuing from the bulb. It soon became clear that the changes of composition followed the discontinuous changes in level. Now, the fundamental condition for this experiment is that a steady state exist in the bulb and that no liquid or vapor be ejected back. For a steady state evaporation, the volume of the liquid in the bulb should remain constant, which condition means that the level with respect to the bulb should be kept invariable. What effect a discontinuous change in level can have upon the composition becomes evident by a simple computation. For example, when the outside liquid contains 50% oxygen the liquid in the bulb has the composition 76% oxygen. If we assume that the liquid stands 3 cm. high in the bulb, and that the calorimeter is suddenly lowered 0.1 mm., then the readjustment of the levels to the previous values will result in the injection into the bulb of liquid of composition different from that already present, producing a decrease of its oxygen content by 0.8%, and at the same time of that of the issuing vapor by an approximately equal amount. Hence we see the importance of lowering the calorimeter at a rate equal, as near as possible, to the rate of descent of the outer level.

A specially constructed mechanism, driven by a direct current motor, maintained a constant rate. It consisted of a series of worms and gears which turned a fixed vertical screw, thus lowering a nut to which the calorimeter was attached. To provide for a wide range of speeds, a variable resistance was inserted in series with the motor armature. In operation the rates of descent of the calorimeter varied from 0.2 to 0.5 mm. per minute. From the physical constants of the liquid, and the dimensions of the calorimeter and Dewar flask, the rate of lowering could be calculated approximately for a definite mixture and power input. The rates of rotation of the vertical screw

were plotted as a function of the two variables, power and composition, thus affording quickly an idea of the proper rate; and the attainment of the exact speed ensued in a short while by adjusting the rheostat and watching the level gauge. By this method, the total change in level during a whole run did not amount to more than a few tenths of a millimeter, thus giving satisfactory constancy of composition and good results for the latent heats.

Gas Measurement.

Coming from the calorimeter, the gas is, of course, perfectly dry and colder than room temperature, so that in passing through the meter it would produce gradual changes in the level of water and the temperature of the meter. It was, therefore, necessary to pass the gas through a conditioning circuit, which could accommodate a flow of two to five liters of gas a minute, consisting of a saturator, a condenser, and a cooling coil. The saturator consisted of a pyrex glass tube, and was kept at 40° or 50° by a heating coil wound on the outside. Then the gas passed through an all-metal condenser, cooled by tap water; and the flow of water could be regulated to maintain the temperature of the gas in issuing from the condenser about 1° higher than the meter temperature. Finally, the gas entered a coil of copper tubing immersed in water, and the temperature of the water was adjusted to keep the temperature of the gas just entering the meter within 0.1° of that of the meter. Temperatures were measured by differential thermocouples of very fine wire, protected from radiation, with one junction in the meter water and the other in constrictions in the pipes.

The laboratory gas meter of the wet type was not adopted without misgiving, for the feeling prevailed that it could not yield a satisfactory degree of precision. The attempt to use a true "rate of flow" meter instead of a semi-integrating type did not meet with success. Waidner and Mueller [12] have made a thorough study of the laboratory gas meters and assert that, if properly used, they are good to 0.2%. With very careful manipulation of the meter, however, our data for the latent heats show a better agreement, indicating a higher precision in use. In addition to the attention paid to the condition of the gas, the meter was carefully leveled before each run, and the water level set with a magnifying glass. The calibrated meter thermometer could be read to 0.05° C. It is possible for the volume of gas

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[12] Bureau of Standards. Technologic Paper, No. 36, 1914.

DANA.

delivered per revolution to depend on the rate of revolution; consequently, the meter must be calibrated as a function of the rate of flow. It is of the utmost importance to perform this calibration so as to prevent this factor from producing an apparent variation of the latent heat with flow.

For the calibration a large tank of over 100 liters in volume, immersed in a vat of water, was filled with dry air at a pressure of two atmospheres. Then the gas was passed at a constant rate, as indicated by an auxiliary flow meter, through the conditioning apparatus and meter exactly as under the conditions of use. From a tall mercury open manometer connected to the tank and read by a cathetometer, and from the barometer readings, the initial and final pressures were determined. Temperatures of the gas in the tank were given by the temperatures of the vat water, allowing, of course, time to reach equilibrium. During a run the temperature of the water did not change more than several hundredths of a degree. Enough gas was passed through the meter to make exactly 35 revolutions of the drum. A number of determinations at several rates of flow were made during two separate calibrations. Unfortunately in the first case, a tank of rather thin sheet metal was used, which, it is now quite certain, became deformed slightly under pressure, with the result that its volume in use differed from that found subsequently by filling with a known volume of water. In the second calibration a much more rigid tank was used. Both calibrations showed about the same variation with flow, but only the second, determined immediately after the main series of latent heat data, is given here.

TABLE III.

CALIBRATION OF METER.

Time per revolution in seconds	Liters per revolution	Mean
90	2.8142	
	2.8156	
	2.8120	2.8139
65	2.8176	
	2.8163	2.8170
55	2.8196	
	2.8218	
	2.8198	
	2.8177	2.8197
45	2.8212	
	2.8230	
	2.8211	
	2.8167	2.8205

The results of this calibration are plotted on Figure 4. All the latent heats are calculated using the value of the meter constant given on the straight line on this plot.
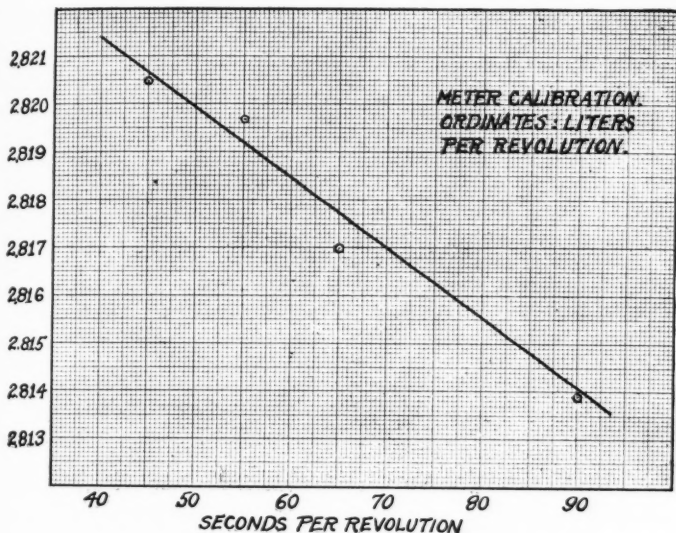

FIG. 4.

ACCESSORY APPARATUS.

For the measurement of the current and potential difference at the heating coil a four-dial White double potentiometer, having a range of 0–50 millivolts, was available. The fifth place was read by deflection of the galvanometer which had a sensitivity of 2.5 mm. per microvolt at 1.25 meters. In all of the measurements the conventional precautions of shielding and of the elimination of stray e.m.f.'s were taken. For the current measurement, the drop across a 0.01-ohm Reichsanstalt standard provided a convenient method. The heating coil was shunted by a 10,000-ohm and 10-ohm Bureau of Standards form of standard resistance, which possessed recent certificates, and the potential taps were on the 10-ohm standard. See Figure 5. Correction, of course, had to be made for the current shunted through

the potential leads and standard coils.   The Weston standard cell for
the potentiometer was compared with two other certified Weston cells,
and the readings of the potentiometer itself were checked by an aux-
iliary potentiometer made up of certified B. S. resistances and standard
cells.   The results of the intercomparison left no doubt that the power
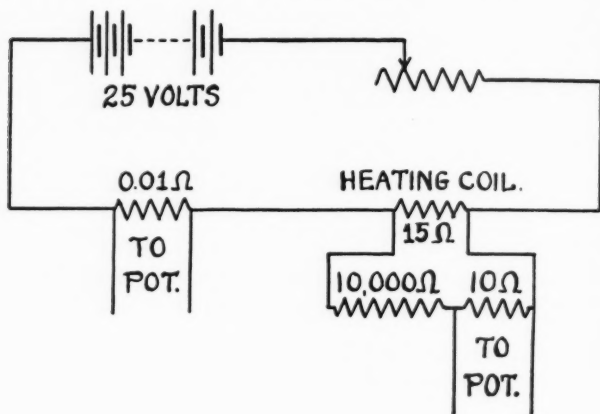was correctly measured in international watts to at least 0.05 %.

<div align="center">Fɪɢ. 5.</div>

The rate of revolution of the meter was determined on a chrono-
graph.   By fastening a projecting piece of platinum foil to the zero
point of the meter, and also covering the needle with foil — this
terminal being grounded to the frame — the time of passing the zero
could be communicated to the chronograph.   Second beats were
furnished by a standard clock, and the position of the meter signal
could be easily read to 0.1 second.   In practice the total time for a
definite number of revolutions, usually in a period of 40 minutes, was
ascertained, giving the mean time per revolution.

For the analysis of the mixtures, an electrical method based on the
thermal conductivities of gases and developed by the Bureau of
Standards,[13] was set up and used as an operating indicator.   Actual
analyses were made by absorbing the oxygen in a copper ammonium

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[13] E. R. Weaver, et al., J. Ind. Eng. Chem., **12**, 359, 1920.

solution in a Hempel pipette.[14]   The range was divided into two parts by using two burettes and the analyses were good to 0.1% of oxygen.   The method of sampling deserves discussion.   It was decided to be best to gather an average sample over a whole run, in order to smooth out possible slight irregularities in the composition resulting from the unsteady motion of the calorimeter.   At the outlet of the meter gas was tapped off at a constant rate by an 8-liter siphon bottle.   A capillary tube flowmeter insured that the same fraction of the issuing gas passed out at any instant.   Instead of using water in the siphon bottle, it was filled with a heavy, white, pure mineral oil in which gases are only very slightly soluble.   However, since the analysis of the sample occurred immediately after collection, all danger from selective solubility was avoided.

LIQUEFACTION OF GASES.

None of the evaporated gas was saved, as the cost and trouble of collecting it would have been far greater than that of using new gas. Electrolytic oxygen, under pressure in 200 cu. ft. capacity cylinders, constituted the source of oxygen.   This gas contained several tenths of a per cent of hydrogen and several tenths of nitrogen; and — it could be assumed with considerable certainty — negligible traces of argon and other rare gases.   The analysis after liquefaction showed usually not more than 0.2% of gases insoluble in the oxygen absorbent. Especially since the liquid was made to boil vigorously before use by the insertion of a metal rod, it should be expected that practically no hydrogen remained.   It could, therefore, be assumed that nitrogen alone constituted the impurity and the small correction necessary was made for it.   We owe to the kindness of Mr. Claude C. Van Nuys of the Air Reduction Company, New York, a number of cylinders of rather pure nitrogen from a liquid air column.   This gas showed less than 0.1% of oxygen and a trace of argon.

A reasonably rapid method of liquefaction was desirable, for two liters of pure liquid had to be prepared for each day's run.   After passing through a reducer and a potassium hydroxide drier, the gas entered under pressure a copper coil immersed in liquid air.   The gas liquefied in the coil and passed out through a double-walled, evacuated, and silvered tube into a Dewar collecting bottle.   When pure oxygen was liquefied by means of liquid containing nitrogen, the liquefied

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[14] W. L. Badger, J. Ind. Eng. Chem., **12**, 164, 1920.

oxygen usually came out colder than corresponded with its boiling
point at atmospheric pressure, and it reached its equilibrium tempera-
ture only after a considerable time. Such liquid could give an errone-
ous latent heat. When, on the other hand, the oxygen was liquefied
with liquid oxygen from a rectifying column, it of course always came
out warmer, but nevertheless quickly reached its proper temperature
because of the cooling produced by evaporation. At any rate, before
any liquid could be used it was equilibrated by the introduction of a
heavy metal rod for a few minutes, thus inducing violent boiling.

Experimental Procedure.

Before each run the calorimeter had to be taken down, the bath
filled with filtered liquid, the calorimeter set up again, and the meter
adjusted. After the start, usually not more than twenty minutes
elapsed before the gas temperatures were in proper adjustment, the
meter water saturated with the gas, and general thermal equilibrium
attained. As a rule, a run at a particular flow lasted about forty
minutes. During the interval periodic readings of current, voltage,
temperatures, pressures, etc., were taken; at the same time, the meter
remained connected to the chronograph record. In the course of a
run, the power fell slowly (not over 0.5% at the most) on account of
the falling e.m.f. of the battery. The other variables might also change
slightly, but since the small variations of the factors were practically
linear, and since these factors enter into the result to the first power,
no error could be introduced by taking a mean value over the whole
period. To show that no irregularities occurred by taking the mean,
the latent heat was calculated on the basis of data recorded over five-
minute periods for an hour. The values thus obtained showed very
little difference among themselves, and the mean of them all agreed
with the total mean.

In order that the same general conditions of operation should exist
for each rate of evaporation, several determinations at different rates
were always made on the same day. In this way, a more accurate
idea of the manner of change of the apparent latent heat with rate
could be acquired. With pure substances, data for three or four rates
in succession were recorded; but when mixtures were used, the longer
time required to reach the correct speed of the screw, and the time
consumed for analysis, left no opportunity to work at more than two
rates per day.

In the case of mixtures, the composition of the liquid in the bath

changed by about 0.6% per hour as a result of heat leaking into it; this leak of course did not enter the calorimeter. Thus, during a run of forty minutes the change in composition amounted to 0.4%. The average sample of the gas took account of this change, and the variation of latent heat with composition is sufficiently small so that no error of consequence from this source was introduced.

RESULTS.

It appeared desirable to adopt one pure substance as a standard, first, to test over a number of months the constancy and reproducibility of the apparatus as a whole for the latent heat, and, second, to be able to test out doubtful points without introducing the complications arising from composition. Accordingly, the latent heat of oxygen was determined off and on for several months.

The formula used to calculate the latent heats from the observed data is as follows:

$$\text{Latent heat} = \left(\frac{Po}{J \; To}\right)\frac{W \; Tm \; t}{D \; N \; Pm} = 0.66504 \; \frac{W \; Tm \; t}{D \; N \; Pm}$$

where

Po = normal atmospheric pressure, 760.0 mm. Hg.

J = electrical equivalent of heat, 1 calorie (15° C) = 4.184 watt-seconds.

To = the absolute temperature of the ice-point, 273.13° C.

W = the mean corrected power in international watts.

Tm = the mean absolute temperature of the gas in the meter.

t = the mean time in seconds per revolution of the meter.

D = the density of the gas passing through the meter, under normal conditions, corrected for gravity.

N = the number of liters of gas delivered per revolution of the meter.

Pm = the mean partial pressure of the gas in the meter.

$Pm = (B + h/13.6 - w)$, where

B = the corrected barometric pressure, in mm. Hg.

h = the excess of pressure in the meter over atmospheric expressed in mm. of water.

w = the pressure of saturated water vapor in mm. Hg at the temperature of the meter.

In deriving the above formula, we have assumed that the laws of perfect gases can be applied to the separate gases and to their mixtures over the ordinary range of room temperature and of atmospheric

pressure.   The latent heats are given in calories (15° C) per gram.[15]
The density for oxygen [16] under normal conditions has been taken as
1.4289, and for nitrogen as 1.2507.   Corrections have been applied
for gravity.   The latent heat depends, of course, on the atmospheric
pressure; but for ordinary fluctuations the effect is small.   The
correction is practically the same for oxygen, nitrogen and mixtures.
It can be calculated from the vapor pressure curve [17] and from the
variation of the latent heat with the temperature.[18]   The effect is
0.0025 calories per gram per mm. Hg.
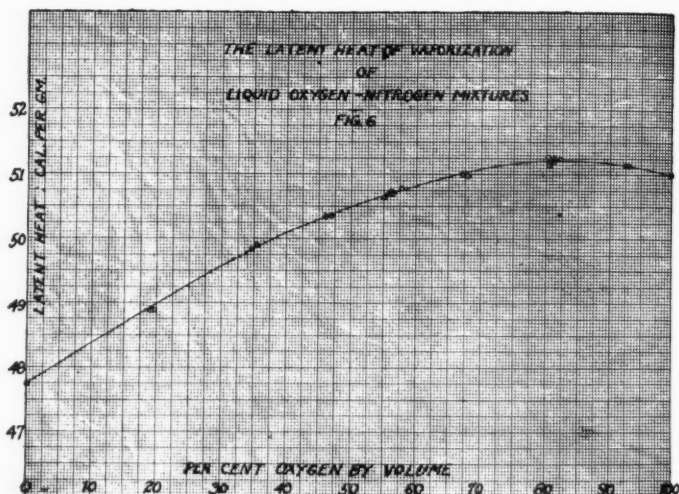
FIG. 6.

In tabulating the final data we will give the itemized mean values
for all the separate factors entering into the latent heat. N, the
number of liters per revolution, can be obtained from Figure 4 by
interpolation of t.   In Table IV are tabulated the final corrected data
for oxygen.   Although the last place in the latent heat is very uncer-

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[15] 1 calorie (15° C) = 4.184 watt-seconds.   See Wärmetabellen der Phys.
Tech. Reichsanstalt, by Holborn, Scheel, and Henning.
[16] Males et Gonzalez, Comptes Rendus, **175**, 6, 1921.
[17] Wärmetabellen, loc. cit., p. 32.
[18] H. Alt, loc. cit.

tain, it has been thought best to include it. The values for nitrogen are given in Table V. In Table VI we list the final observed values for the latent heats of mixtures of various compositions and at different rates of evaporation. These results are plotted on Figure 6.

TABLE IV.

THE LATENT HEAT OF VAPORIZATION OF OXYGEN AT 1 ATMOSPHERE.

Date	Cal. no.	W	Pm	Tm	t	Latent heat 15° Cal.
Nov. 16	VI	8.507	745.9	293.06	92.171	50.981
1921		10.202	746.0	293.33	76.818	50.954
		13.587	746.1	293.64	57.701	50.970
		19.145	746.2	293.86	40.956	50.967
Dec. 1	VI	8.522	740.7	295.75	90.674	51.048
		10.219	740.7	296.02	75.596	51.042
		13.635	741.1	296.13	56.661	50.989
		19.948	741.5	296.28	38.772	50.997
Dec. 3	III	8.711	738.2	293.74	88.934	50.985
		10.164	738.4	293.80	76.274	50.984
		13.482	738.6	293.84	57.581	50.998
		19.813	738.6	293.86	39.242	51.032
Dec. 7	III	8.561	740.5	293.83	91.068	51.000
		10.161	740.7	293.00	76.800	51.030
		10.109	740.9	293.17	77.132	51.004
		13.348	740.9	293.31	58.427	50.990
		19.832	741.3	293.44	39.423	51.063
Feb. 13	VI	8.188	744.0	293.07	95.577	51.017
1922		11.050	745.3	293.13	70.960	50.978
		14.629	746.5	293.19	53.774	51.029
Feb. 16	VII	8.394	741.3	292.97	93.096	51.065
		11.101	741.6	293.08	70.372	51.000
		16.175	742.1	293.25	48.383	51.021
					Mean Value	51.006

As indicated before, we could by taking temperature measurements in the bulb and in the bath obtain the temperature-composition diagram for oxygen-nitrogen mixtures at atmospheric pressure. Unfortunately, this was not done except for two mixtures, for it was

TABLE V.

THE LATENT HEAT OF VAPORIZATION OF NITROGEN AT 1 ATMOSPHERE.

Date	Cal. no.	W	Pm	Tm	t	Latent heat 15° Cal.
Oct. 3	III	10.073	734.7	293.12	62.922	47.704
1921		15.069	734.3	293.28	42.118	47.767
Jan. 20	VI	7.860	748.8	293.83	81.806	47.685
1922		10.532	749.0	293.98	61.134	47.709
		13.837	749.3	294.03	46.578	47.709
Feb. 23	VI	7.900	740.9	291.53	81.434	47.813
		10.964	738.5	291.87	58.464	47.787
		15.181	737.7	292.08	42.204	47.181
April 10	VI	7.901	734.6	293.48	80.045	47.711
		10.290	734.2	293.66	61.427	47.693
		14.379	733.7	293.74	43.983	47.720
					Mean Value	47.737

expected that the data would be secured from other sources to a higher degree of precision than could be readily obtained in our investigation. The temperature readings in Table VII were made with copper-constantan couples of fine wire placed in calorimeter VI. A single-junction couple, inserted in the central tube, had its junction in the liquid in the bulb, while a double-junction couple, strapped to the outside of the calorimeter, gave the temperature of the bath. While liquid oxygen and liquid nitrogen were being evaporated in the calorimeter, the couples were calibrated in place; in addition, the e.m.f.'s at the boiling point of water and at the transition temperature of sodium sulphate were found. For the boiling points of oxygen and nitrogen, we chose the latest values determined at Leiden.[19] ΔT signifies the vertical temperature difference between the two curves in the $T-x$ diagram, Figure 3. For comparison we include the values determined by Baly.[20] It is believed that our values are good — relatively at least — to 0.03° C. That there are disagreements between these and Baly's results is evident here and also in some preliminary work by the late Mr. A. K. Dunbar on the oxygen-nitrogen equilibrium diagram in which departures in the same direction were found.

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[19] Comm. Leiden, No. 152, d. P. G. Cath.
[20] Baly, Phil. Mag., **49**, 517, 1900.

TABLE VI.

The Latent Heat of Vaporization of Liquid Oxygen-Nitrogen Mixtures at 1 Atmosphere.

Date	Cal. no.	W	Pm	Tm	t	Comp. % oxygen	Latent heat 15° Cal.
Feb. 21	VI	8.400	755.6	293.46	92.606	80.25	51.280
1922		11.050	754.9	293.80	70.376	81.2	51.254
		15.500	754.8	294.00	50.223	82.1	51.237
Feb. 24	VI	8.063	752.0	292.63	94.168	67.0	51.007
		14.908	752.5	292.97	51.032	67.9	50.968
Feb. 25	VI	8.187	752.0	292.60	90.638	54.9	50.637
		10.889	751.6	292.68	68.275	55.6	50.665
		14.825	751.9	292.86	50.282	56.1	50.731
Feb. 27	VI	7.928	743.5	293.40	90.708	46.0	50.346
		14.927	743.8	293.74	48.307	46.85	50.352
Feb. 28	VI	7.997	746.1	293.34	84.447	18.85	48.867
		14.104	747.0	293.43	48.076	19.4	48.894
Mar. 6	VI	8.127	747.4	293.10	96.054	92.5	51.154
		14.874	747.2	293.47	52.539	92.8	51.147
Mar. 22	VI	7.950	742.1	292.56	88.289	34.6	49.837
		14.374	742.5	292.97	49.002	35.4	49.900
Mar. 27	VII	7.831	751.1	293.88	94.568	56.6	50.710
		15.110	750.6	294.16	49.171	57.6	50.773
Mar. 28	VII	8.341	742.3	293.89	91.344	80.4	51.156
		15.040	741.4	294.32	50.729	81.1	51.212

TABLE VII.

Temperature Measurements.

Composition % oxygen	Outside This research	Outside Baly	In bulb This research	In bulb Baly	ΔT This research	ΔT Baly
Pure oxygen	90.13	90.96	90.13	90.96	0	0
46.7	81.10	81.36	85.20	85.32	4.10	3.96
34.6	79.96	80.12	83.58	83.68	3.62	3.56
Pure nitrogen	77.31	77.54	77.31	77.54	0	0

Discussion of Results.

In any calorimetric experiment the problem of heat leaks and other thermal disturbances provides the chief source of difficulties and errors. In this research we have first of all tried by design to avoid these troubles; in the second place, to make, as far as practicable, independent measurements of possible heat leaks; and, thirdly, to regard the final results — considered particularly as a function of the rate of evaporation — as criteria of the absence of irregularities. The first two factors have been previously considered. As to the latter, the most thorough tests were made with liquid oxygen, and it was assumed and borne out by the results that the same conclusions held for nitrogen and mixtures. If the extraneous influences such as conduction, convection, radiation, superheating of liquid and vapor, and spattering and carrying of spray enter into the experiment, then it can be shown that the manner of variation of the latent heat with the rate of evaporation should throw some light on the degree to which these influences enter. In general, the curve will not be a straight line. An examination of the final results discloses small variations with flow in different directions, but with a tendency towards a minimum; in no case, nevertheless, is the difference between two results in a single run more than 0.15 %. We conclude that the measurements show the effect on the average to be less than the experimental error or less than 0.1 %. To be able to judge accurately of the presence of disturbing factors, measurements of higher absolute precision than the magnitude of these are required. For example, suppose that a constant leak of 0.2 % existed at the lowest flow; then by increasing the rate by 100 %, the observed latent heat would change only by 0.1 %.

The average deviation of the mean of twenty-three determinations of the latent heat of oxygen is 0.025 calories per gram or 0.05 %. The average deviation from the mean of eleven determinations for nitrogen is 0.042 calories per gram or 0.09 %. From a large-scale drawing of Figure 6, the deviations of the points from the curve have been estimated; the average amounts to about 0.03 calories per gram or 0.06 %. If we consider the precision and accuracy to which the separate factors involved in the latent heat have been measured, we can get an idea of the accuracy of the final results. In Table VIII, the errors are estimated — with experience and calibrations as a basis — in per cent of the latent heat. From this table we conclude that the results should be accurate in absolute measure to about 0.2 %, and relative to themselves to about 0.1 %. It is to be observed that a large amount of

TABLE VIII.

ESTIMATION OF ERRORS.

Factor	Accidental error or deviation from mean	Maximum possible systematic error	Maximum probable systematic error
W	0.03 %	0.05 %	0.03%
Tm	0.03	0.05	0.03
t	0.01	0.02	0.01
D	0.01	0.02	0.015
N	0.05	0.20	0.10
Pm	0.015	0.05	0.02
Heat leaks or other effects	—	0.15	0.10

preliminary data has been taken, although not recorded here, which fully substantiates the final values.

What has been measured in this investigation is the difference in heat-contents ($H = E + pv$) between the liquid state of a mixture and the vapor state of the same composition vertically above it on the temperature-composition diagram. If we knew the heat of mixture of the liquids, we should be able to determine the $H - x$ diagram for liquids. The heat-contents obtained in this investigation then allow us to get the $H - x$ diagram for the vapors. A knowledge of both of these curves and of their difference seems to be fundamental in ascertaining the numerous possible latent heats of a mixture.

Now, we can devise an hypothetical process which, starting from the initial state 1 (Fig. 3), will finally lead to the state 1'; and since the change in heat-content is independent of the path, we can obtain a possible expression for the change in heat-content from 1 to 1'. This circuitous path provides a clearer insight into the evaporation process and shows that we may be able to procure information other than the latent heat from the experiment.

The process is to be carried out in four main steps by means of an hypothetical thermodynamic engine, shown in Figure 7. Starting with the main chamber filled with a mixture containing x moles of liquid oxygen and $(1 - x)$ moles of liquid nitrogen at the temperature T_1 (Fig. 3), and, assuming that the semi-permeable membrane M_1 is permeable to liquid oxygen alone while the membrane M_2 is permeable to nitrogen alone, the membranes are then pushed in, separating the oxygen and nitrogen. This first step is to be performed isothermally at T_1, at the same time allowing the liquid oxygen to remain at its saturation pressure P_O, corresponding to T_1, and the nitrogen at
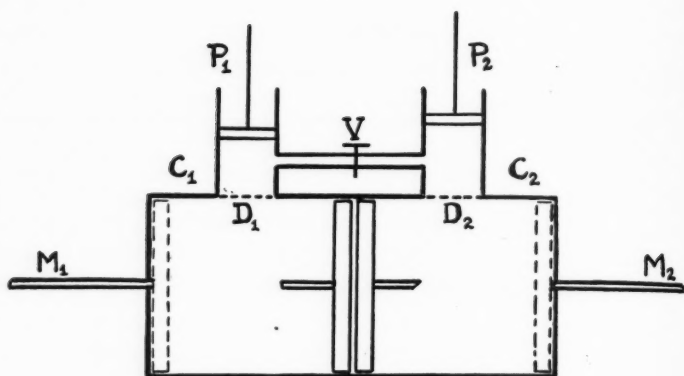
FIG. 7.

its saturation pressure P_N, corresponding to T_1. Secondly, x moles of oxygen are evaporated at T_1 and P_O by removing the diaphragm at D_1, pulling out the piston P_1, and adding the necessary heat. Similarly, $(1 - x)$ moles of liquid nitrogen are evaporated at T_1 and P_N. Thirdly, x moles of oxygen vapor are superheated in chamber C_1, from T_1 to $T_{1'}$ at P_O' (Fig. 3); and $(1 - x)$ moles of nitrogen vapor are superheated from T_1 to $T_{1'}$ at P_N. Finally the oxygen is compressed from pressure P_O to atmospheric at $T_{1'}$; and the nitrogen is expanded from P_N to atmospheric at $T_{1'}$. Then the valve V is opened, and the gases are allowed to mix at $T_{1'}$, while the pressure is maintained at atmospheric.

The expressions for the change in heat-content for the individual steps can be written down, but all the terms cannot be evaluated because of the lack of thermodynamic data.

I. $H = E + pv.$ $dH = dE + p\ dv + v\ dp.$ $\int dH = \Delta_1 H$

Then

$$\Delta_1 H = x \int_{P=1}^{P=P_O} \left\{ v - T \left(\frac{\partial v}{\partial T} \right)_p \right\} dp$$

$$+ (1 - x) \int_{P=1}^{P=P_N} \left\{ v - T \left(\frac{\partial v}{\partial T} \right)_p \right\} dp - Q_M$$

The first two terms represent the "work" terms measuring the heat-content required to bring the liquid components from atmospheric

pressure to slightly above atmospheric for nitrogen, and slightly below for oxygen; consequently these terms tend to cancel. We will denote them by W. To evaluate them we need to know the equations of state for the liquids. Q_M represents the heat of mixture of x moles of liquid oxygen and $(1 - x)$ moles of nitrogen at T_1. Thus $\Delta_1 H = W - Q_M$.

II. $p =$ constant; hence $v\,dp = o$, and $dH = dE + p\,dv = dQ$

Denoting by L_O and L_N the latent heats of the individual components at T_1, we get

$$\Delta_2 H = \int dQ = x\,L_O + (1 - x)\,L_N$$

III. $dH = dE + p\,dv = dQ = C_p\,dT$

$$\Delta_3 H = \int dQ = x \int_{T_1}^{T_{1'}} C_{po}\,dT + (1 - x) \int_{T_1}^{T_{1'}} C_{p_n}\,dT$$

where C_{po} and C_{p_n} are the specific heats at constant pressure of oxygen and nitrogen vapors respectively. Since the specific heats at constant pressure do not vary rapidly with the temperature or pressure, they can be taken as constants over the range T_1 to $T_{1'}$ — which is not more than $5° \text{C}$ — and they can be assumed equal to their values at atmospheric pressure. The largest step in heat-content is in step II, and since III does not amount to more than 2% of II, the above approximations are justified.

$$\therefore \ \ \Delta_4 H = x\,C_o(T_{1'} - T_1) + (1 - x)\,C_n\,(T_{1'} - T_1)$$

IV. We get expressions similar to those in I.

$$\Delta_4 H = x \int_{P=P_O}^{P=1} \left\{ v - T\left(\frac{\partial v}{\partial T}\right)_p \right\} dp$$
$$+ (1 - x) \int_{P=P_N}^{P=1} \left\{ v - T\left(\frac{\partial v}{\partial T}\right)_p \right\} dp + q_m$$

where q_m is the heat of mixture of the vapors at $T_{1'}$. As before, the the first two terms tend to cancel. Denote them by w. Then $\Delta_4 H = w + q_m$. For ideal gases $\Delta_4 H$ would vanish.

The net change in heat-content for all the steps is

$$\Delta H = \Delta_1 H + \Delta_2 H + \Delta_3 H + \Delta_4 H$$
$$\Delta H = W + w - Q_m + q_m + x\,L_o + (1 - x)\,L_N$$
$$+ x\,C_o\,(T_{1'} - T_1) + (1 - x)\,C_n\,(T_{1'} - T_1)$$

Thus the sum of all these terms should be equal to the latent heat found in this investigation. At the present time we cannot evaluate the first four terms. To evaluate the remainder, it is obvious that we must know the temperature-composition diagram. A preliminary calculation of these terms has been made using Baly's data, and the best data that could be found for specific heats and the variation of latent heat with temperature, with the result that the calculated curve of latent heats falls not more than 0.1 % from the experimental curve. We can probably conclude that the sum of the first four terms in ΔH is of the order of 0.1 %. Thus from the last equation we have a method of calculating from the individual latent heats and specific heats of the vapors the latent heats of the mixtures with an accuracy probably at least as good as that of the experimental determinations on the mixtures.

The reason for the maximum in the latent heat curve, Figure 6, becomes evident on referring back to the previous discussion. The latent heat terms alone when plotted against composition form very roughly a straight line. On adding the terms for the superheating of the vapor, the curve acquires a maximum. Thus no peculiar physical significance is to be attached to this maximum.

SUMMARY.

A new calorimeter has been designed for the determination of the latent heats of vaporization at low temperatures of pure liquids and their binary mixtures. The calorimetric method adopted is the continuous flow method at constant pressure. A latent heat has been defined and measured which involves the change in heat-content from the liquid state to the vapor state vertically above it on the vapor line in the temperature-composition diagram.

The latent heat of vaporization of liquid oxygen at one atmosphere has been found to be 51.01 calories [21] (15° C) per gram, while that of liquid nitrogen has been determined as 47.74 calories per gram. In the following table (p. 267) are given the values of the latent heats of the mixtures which were read from a smooth curve drawn through the experimental points.

The absolute accuracy of the results is estimated as not less than 0.2 %, while the shape of the curve is believed to be good to 0.1 %.

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[21] 1 calorie (15° C) assumed equal to 4.184 international watt-seconds.

TABLE IX.

THE LATENT HEAT OF VAPORIZATION OF LIQUID OXYGEN-NITROGEN MIXTURES AT 1 ATMOSPHERE.

Per cent oxygen	Latent heat	Per cent oxygen	Latent heat
0	47.74	55	50.67
5	48.06	60	50.83
10	48.37	65	50.97
15	48.68	70	51.08
20	48.98	75	51.17
25	49.28	80	51.23
30	49.57	85	51.23
35	49.83	90	51.18
40	50.07	95	51.12
45	50.28	100	51.01
50	50.48		

A few observations on the temperature-composition diagram are also given. With the aid of data on the individual latent heats and on the specific heats of the superheated vapors it is shown to be possible to calculate the latent heats of the mixtures, with probably a high accuracy.